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Retention of pesticide Endosulfan by nanofiltration: Influence of organic matter-pesticide complexation and solute-membrane interactions

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1 Abstract

2 Nanofiltration (NF) is a well-established process used in drinking water production to effectively
3 remove Natural Organic Matter (NOM) and organic micropollutants. The presence of NOM has
4 been shown to have contrasting results on micropollutant retention by NF membranes and removal
5 mechanisms are to date poorly understood. The permeate water quality can therefore vary during
6 operation and its decrease would be an undesired outcome for potable water treatment. It is hence
7 important to establish the mechanisms involved in the removal of organic micropollutants by NF
8 membranes in the presence of NOM. In this study, the retention mechanisms of pesticide
9 Endosulfan (ES) in the presence of humic acids (HA) by two NF membranes, TFC-SR2 and TFC-
10 SR3, a "loose" and a "tight" membrane, respectively, were elucidated. The results showed that two
11 mechanisms were involved: (1) the formation of ES-HA complexes (solute-solute interactions),
12 determined from solid-phase micro-extraction (SPME), increased ES retention, and (2) the
13 interactions between HA and the membrane (solute-membrane interactions) increased membrane
14 molecular weight cut-off (MWCO) and decreased ES retention. HA concentration, pH, and the ratio
15 between micropollutant molecular weight (MW) and membrane MWCO were shown to influence
16 ES retention mechanisms. In the absence of HA-membrane interactions at pH 4, an increase of HA
17 concentration increased ES retention from 60% to 80% for the TFC-SR2 and from 80% to 95% for
18 the TFC-SR3 due to ES-HA complex formation. At pH 8, interactions between HA and the loose
19 TFC-SR2 increased the membrane MWCO from 460 to 496 g/mol and ES retention decreased from
20 55% to 30%, as HA-membrane interactions were the dominant mechanism for ES retention. In
21 contrast, for the "tight" TFC-SR3 membrane the increase in the MWCO (from 165 to 179 g/mol),
22 was not sufficient to decrease ES retention which was dominated by ES-HA interactions.
23 Quantification of the contribution of both solute-solute interactions and solute-membrane
24 interactions is hence fundamental in understanding the removal mechanisms of micropollutant by
25 NF membranes in the presence of NOM in order to optimize the treatment process.

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Keywords: nanofiltration, micropollutant, natural organic matter, solute-solute interactions, solute-membrane interactions

1. Introduction

Removal of organic micropollutants from water intended for human consumption is a growing concern for the drinking water industry due to increasing occurrence of these compounds in surface water and groundwater, as well as their adverse effects on human health (Schwarzenbach et al. 2006). Application of nanofiltration (NF) processes for the removal of micropollutants has become widespread due to an effective rejection achieved by full scale plants (Cyna et al. 2002) and the extensive research carried out in explaining the micropollutant removal mechanisms (Bellona et al. 2004, Van der Bruggen et al. 2006).

Natural organic matter (NOM) is ubiquitously present in water and it influences the fate and the behaviour of micropollutants and their removal by NF (Plakas and Karabelas 2009, Salvaterra et al. 2011). NOM has shown to increase, decrease or have negligible effect on micropollutant removal by NF (Agbekodo et al. 1996, Devitt et al. 1999, Jin et al. 2007, 2010, Plakas et al. 2006, Xu et al. 2005). Contrasting results have been attributed to the different types of micropollutants, membranes and organic matter used in previous studies and to the complexity of the retention mechanisms (Bellona et al. 2004, Boussahel et al. 2002, Jin et al. 2007, Sanches et al. 2011).

The increase of micropollutant retention in the presence of NOM has been attributed to the formation of micropollutant-NOM complexes of bigger size and higher charge compared to the micropollutant on its own (Agbekodo et al. 1996, Boussahel et al. 2002, Devitt et al. 1999, Jin et al.

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2007, 2010, Plakas et al. 2006, Schäfer et al. 2010). Jin et al. (2007) attempted to estimate estrone removal by NF in the presence of humic acids (HA) using the percentage of the fraction of estrone bound to HA from literature. Poor estimation was attributed to the difference in estrone concentration between the experiments and the literature. Jin et al. (2007) also inferred that most of the estrone-HA interactions took place on the membrane rather than in solution, explaining further the poor removal estimation. Neale and Schäfer (2012) were able to quantify the contribution of hormone-HA interactions on increased hormone removal by ultrafiltration (UF) in the presence of HA by determining organic matter-water partition coefficients. Increasing HA concentration led to more hormone partition onto HA and in turn to greater hormone removal by UF, demonstrating the role of micropollutant-NOM interactions on micropollutant removal. Increase of micropollutant removal by NF in the presence of NOM was also attributed to the modification of the membrane surface caused by adsorption of NOM. NOM deposition can cause pore clogging and change membrane surface charge, resulting in improved retention by steric and electrostatic mechanisms (Jin et al. 2007, Xu et al. 2005).

Several mechanisms have been inferred to explain reduced or similar retention of micropollutants in the presence of NOM. Lack of binding between the studied micropollutants and NOM was considered the reason for unchanged retention (Boussahel et al. 2002, Jin et al. 2007, 2010). Reduced micropollutant retention was attributed to increased membrane molecular weight cut-off (MWCO) caused by the presence of organic matter (Xu et al. 2005, Xu et al. 2006). Organic matter has been shown to enhance the negative charge of NF membranes, so it was inferred that the increased electrostatic repulsion within the membrane pores increased membrane MWCO (Braghetta et al. 1997, Childress and Elimelech 1996). Schäfer et al. (2010) inferred that membrane hydrophilization might be responsible for the observed reduction in estrone removal when organic matter was present and for the increase in pure water flux after organic matter filtration. The decrease in micropollutant retention in the presence of organic matter was observed for "loose"

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membranes (*i.e.* membrane whose MWCO is bigger than micropollutant molecular weight, MW) (Schäfer et al. 2010, Xu et al. 2005, Xu et al. 2006). From the literature, it can be hypothesized that a correlation might exist between micropollutant removal mechanisms in the presence of NOM and micropollutant MW/membrane MWCO ratio. In the cited studies, the mechanisms responsible for reduced micropollutant retention in the presence of NOM were presented as hypotheses without being quantified, indicating the need to perform thorough investigations to demonstrate for which conditions the mechanisms apply.

For micropollutants that adsorb onto the membranes, retention decreases with time until the membrane is saturated with the compound and real retention is reached (Kimura et al. 2003, Nghiem et al. 2004, Semiao and Schäfer 2011). In some case studies there is no indication that membrane saturation was achieved. If the membrane is not saturated with the compound, retention can therefore be overestimated and the comparison of retention results with and without NOM can lead to erroneous conclusions. For example, lower micropollutant retention in the presence of NOM has been linked to adsorption competition on the membrane between the micropollutant and NOM. When NOM is present, it adsorbs on the membrane and decreases the membrane adsorption sites available for the micropollutant. It was therefore inferred that the decrease in micropollutant adsorption in the presence of NOM caused a lower retention of the same micropollutant (Yoon et al. 2006). Vice versa, higher micropollutant adsorption was inferred to cause lower retention because adsorbed micropollutants might experience higher diffusion to the permeate side (Boussahel et al. 2002). These two opposing results might be linked to the above-mentioned lack of saturation of the membrane by the micropollutant. It is hence important to ensure membrane saturation during the experiments in order to be able to compare retention results in the presence and absence of NOM. These findings reflect the complexity of the mechanisms involved in the removal of micropollutants by NF membranes in the presence of NOM and invite a systematic investigation of NOM influence on micropollutant removal.

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Three main mechanisms can influence micropollutant retention by NF in the presence of NOM: solute-solute interactions, solute-membrane interactions and solute-foulant interactions. The impact of fouling by NOM on micropollutant retention has been extensively studied (Hajibabania et al. 2001, Ng and Elimelech 2004, Plakas et al. 2006, Xu et al. 2006), so it was not further investigated in this study.

In this work, commercial HA have been chosen as a representative of the bigger fraction of NOM because they have been extensively characterized in the literature and they were shown to have similar organic matter retention properties than real Scottish NOM (Chin et al. 1994, De Munari 2012, Shin et al. 1999). Pesticide Endosulfan (ES) has been employed as a model micropollutant because it is believed to interact with NOM and it is neutral over a large pH range (Banasiak 2009, Forman et al. 1965). Moreover, ES is extensively used worldwide, persistent in the environment, toxic to aquatic life and has estrogenic properties similar to DDT (German Federal Environment Agency 2007, Soto et al. 1994). Two commercial NF membranes, TFC-SR2 and TFC-SR3 provided by Koch, have been selected as their MWCO is respectively higher and lower than the ES molecular weight (MW).

The aim of this study is to elucidate the mechanisms responsible for the different retention trends obtained for the micropollutants in the presence of NOM. The objectives were to: (1) quantify the contribution of solute-solute interactions (*i.e.* formation of ES-HA complexes) on ES removal; (2) investigate the contribution of ES-membrane interactions on ES retention; and (3) investigate the contribution of HA-membrane interactions on ES retention for a "tight" and a "loose" membrane. For the first time, the relative contribution of solute-solute interactions and solute-membrane interactions to micropollutant retention by NF membranes in the presence of organic matter will be evaluated to explain micropollutant retention mechanisms.

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In order to quantify the influence of solute-solute interactions on ES retention, the method developed by Neale and Schäfer for UF (2012) was adapted to NF and applied to quantify the contribution of ES-HA complexes on ES removal. HA-water partition coefficient K_{HA} for ES was determined and the calculated fraction of ES bound to HA was used to estimate ES removal due to complex formation. Neale and Schäfer (2012) did not consider the contribution of solute-membrane interactions since the dominant mechanism for hormone removal by UF was deemed to be solute-solute interactions only. In this study, the contribution of solute-membrane interactions on micropollutant retention was investigated by evaluating ES adsorption to the membranes (ES-membrane interactions) and the influence of HA on membrane characteristics (HA-membrane interactions).

2. Materials and methods

2.1 Stirred cells equipment and filtration protocol

Experiments were performed with a stainless steel stirred cell with a volume of 990 mL and a diameter of 70 mm, resulting in a membrane area of 38.5 cm². The cell was pressurised at 5 bar with filtered lab air to create similar conditions as full scale membrane plants; the pressure was kept constant and automatically measured every minute with a pressure transducer (Omega Engineering, UK). Temperature inside the cell and permeate collected on an electronic balance (Advancer Pro, Ohaus, UK) were measured every minute. A digital magnetic stirrer (Fisher Scientific, UK) was used at a speed of 300 rpm.

Membrane coupons were compacted for an hour at 15 bar and pure water flux was measured at 5 bar, before and after the experiments. A 900 mL feed solution was prepared prior to the experiments and stirred at 150 rpm for 24 hours to ensure formation of ES-HA complexes. The experiments

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were carried out in concentration mode in two phases. In the first phase, 480 mL of feed were filtered in order to ensure membrane saturation by ES, where a feed, a permeate and a concentrate sample were collected to determine ES sorption by mass balance. Filtration of 480 mL of solution was determined as sufficient to reach ES saturation for both membranes. In the second phase, the permeate was returned to the stirred cell, a feed, a concentrate and four permeate samples of 60 mL each were collected. Mass of ES sorbed to the membranes was determined with a mass balance on the total solution filtered during the experiment and no adsorption of micropollutant occurred during the filtration of the 4×60 mL. Retention was determined with a mass balance on the last permeate collected; retention was constant for the last four permeates since equilibrium had been reached.

2.2 Membrane characteristics

TFC-SR2 and TFC-SR3 membranes provided by Koch Membrane Systems (San Diego, USA) were extensively characterized. Membrane MWCO was determined by filtering aqueous solutions containing dioxane, xylose, dextrose and polyethylene glycol (PEG) of different MW (Teixeira et al. 2005). Pore radius was estimated using the hydrodynamic model (Nghiem et al. 2004). Point of zero charge was measured with an electrokinetic analyser (EKA, Anton Paar KG, Austria) with the same background electrolyte used in the experiments. TFC-SR2 and TFC-SR3 membranes are amphoteric, positively charged at acidic pH and negatively charged with increasing pH. Contact angle measurements (CAM 100, KSV Instrument Ltd, US) were performed using the sessile drop method. At least three measurements per membrane were performed and the average of the measurements is reported (standard deviation $\pm 2^\circ$). In the case of membranes with HA deposits, which presented zones of different colour, measurements were repeated in triplicate for different zones and the average was reported. The variation between different zones of the membranes with HA deposit was $\pm 2^\circ$, comparable with the variation obtained by repeated measurements on virgin membranes. Roughness was estimated by atomic force microscopy (AFM) using a multimode AFM

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system (VEECO, presently Bruker Corporation, USA) by contact mode in liquid (scan size 2.0×2.0 μm). The cantilever (Mikromasch CSC38/AIBS type B) was made of Si with a tip radius of 10 nm.

Since a new membrane coupon was used for each experiment, the reproducibility of retention and adsorption results was mainly affected by the variability of different membrane coupons. For quality control, only coupons with a pure water flux varying ±15% were employed in the experiments.

2.3 Chemicals and solution chemistry

Experiments were conducted in ultra-pure water obtained by PuraLab Ultra (Elga LabWater, UK). All chemicals were of analytical grade. Inert organics for MWCO and pore size determination consisted of 25 mgC/L of dioxane, dextrose PEG 400, PEG 600, PEG 100 (Fisher Scientific, UK) and xylose (Acros Organics, UK). HA (Sigma Aldrich, UK) stock solutions containing 250 mgC/L were conserved in the fridge in the dark for one week maximum. HA was used at a concentration of 12.5 mgC/L because it represents typical NOM concentration found in upland natural water in Scotland (De Munari 2012). Experiments with HA ranging from 5 to 250 mgC/L were performed to study the effects of HA concentration on ES-HA complex formation. Background electrolyte solution consisted of 1 mM NaHCO₃ and 20 mM NaCl (Fisher Scientific, UK). pH was adjusted with 1M of HCl or NaOH (Fisher Scientific, UK). Radiolabeled [2,3-¹⁴C] ES (>95% purity; 18.5 MBq solid form) was purchased from the Institute of Isotopes Co., Ltd. (Hungary). Feed solutions of 10 μg/L of radiolabeled ES were prepared from stock solutions (10,000 μg/L) made in methanol (CH₃OH) (Fisher Scientific, UK).

ES is an organochloride insecticide of the cyclodiene group commercially produced as a 7:3 isomeric mixture of α and β forms (Table 1). ES isomers degrade by chemical hydrolysis to ES-diol at pH > 8 with half time of less than 12 hours (Peterson and Batley 1993), comparable with the time

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used in the filtration experiments. ES-sulfate can also be a hydrolysis product of ES isomers in the presence of microbiological activity or strong chemical oxidants but it was not detected in "artificial" samples after eight weeks (Peterson and Batley 1993). Therefore, it was inferred that ES-sulfate was not present in the solutions prepared for the experiments.

(TABLE 1)

2.4 Analytical methods

Radiolabeled ES was measured with a liquid scintillation counter (Beckman LS 6500, USA); 1mL of sample was analysed in 20 mL scintillation vials containing 7 mL of scintillation liquid (Ultima Gold LLT, UK). Inert organics (dioxane, dextrose PEG 400, PEG 600, PEG 100) were measured with a Total Organic Carbon (TOC) V_{CPH/CPN} Shimadzu analyser with the high sensitivity catalyst in a non-purgeable organic carbon mode. Calibration standards were made using potassium hydrogen phthalate (Acros Organics, UK). Samples were analysed for TOC the same day of the experiments. HA concentration was determined by ultraviolet absorbance at 254 nm measured with an UV Visible Spectrophotometer Cary 100 (Varian, UK). Samples were analysed within a few hours from collection and stored in the dark at controlled room temperature. Conductivity and pH measurements were conducted for the feed, permeate and concentrate samples using a pH/Cond 340i meter (WTW, Germany).

2.5 Calculation of HA-water partitioning coefficient K_{HA}

HA-water partitioning coefficient K_{HA} for ES was determined as a function of pH and HA concentration using the negligible-depletion solid phase micro-extraction (nd-SPME) method developed by Neale et al. (2008). The SPME method allows estimating the fraction of micropollutant bound to NOM, irrespective of the specific interactions (e.g. hydrophobic, hydrogen bonding, etc.) between micropollutant and NOM. The method measures the freely dissolved

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concentration of a micropollutant in water at equilibrium and it is based on the valid assumption

that only the freely dissolved micropollutant and not the fraction bound to the organic matter is measured by the SPME fibre (Poerschmann and Kopinke 2001).

The SPME fibres were calibrated to establish the time necessary to reach equilibrium and calculate the fibre-water partition coefficient K_{fw} for ES as a function of pH. Seven polyacrylate (PA) fibres (Polymicro Technology, US) of 5 cm length each were introduced in 100 mL solutions containing 10, 25, 50, 100 µg/L of ES and background electrolyte (1 mM NaHCO₃ and 20 mM NaCl) with pH varying from 4 to 12. The fibres were shaken at 200 rpm at 25 °C in a Certomat BS-1 incubator shaker (Sartorius, Germany) and extracted at regular time intervals. The fibres were cut into three pieces, added to a scintillation vial with 7 mL of scintillation liquid, manually shaken and left overnight to desorb before being analysed by scintillation counter to determine m_F , the mass of ES in the fibre.

A kinetic approach was used to quantify K_{fw} :

$$K_{fw} = \frac{C_F}{C_W} = \frac{m_F}{m_W} \cdot \frac{V_W}{V_F} \quad (1)$$

where C_F (µg/L) is the concentration of ES in the fibre, C_W (µg/L) is the concentration of freely dissolved ES in aqueous solution, m_W (µg) is the mass of freely dissolved ES in aqueous solution as sampled at the end of the experiments, V_W (L) is the volume of the aqueous solution, V_F (L) is the volume of the fibre (0.77 µL). Log K_{fw} was calculated from the linear regression of log C_F as a function of log C_W obtained with the four different concentrations of ES in solution.

In order to determine the HA-water partitioning coefficient K_{HA} for ES as a function of pH and HA concentration, 100 mL solutions containing 10, 25, 50, 100 µg/L of ES, 5, 12.5, 50, 125, 250 mgC/L of HA and background electrolyte were prepared at pH varying from 4 to 12 and shaken for 24

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hours at 200 rpm to allow complex formation. Fibres were then introduced in the solution and

shaken for 96 hours, chosen as equilibrium time. Following, the fibres were extracted, cut into three pieces, added to a scintillation vial with 7 mL of scintillation liquid, manually shaken and left overnight to desorb before being analysed by scintillation counter to determine m_F .

In the presence of HA, m_W was determined from the ES-fibre partitioning coefficient, K_{fw} , obtained during fibre calibration as follows:

$$m_W = \frac{m_F}{K_{fw}} \cdot \frac{V_W}{V_F} \quad (2)$$

K_{HA} (L/kg) was then calculated as:

$$K_{HA} = \frac{c_{HA}}{C_W} = \frac{m_{HA}}{m_{DOM}} \cdot \frac{V_W}{m_W} \quad (3)$$

where c_{HA} (µg/kg) is the concentration of ES sorbed to HA, m_{HA} (µg) is the mass of ES sorbed to HA, m_{DOM} (kg) is the total mass of HA dissolved in solution.

In order to estimate m_{HA} a full mass balance was carried out:

$$m_{HA} = m_{TOT} - m_F - m_W \quad (4)$$

where m_{TOT} is the initial mass of ES in solution before the fibre is added.

The fraction of ES bound to HA f_{HA} (%) was determined as (Neale and Schäfer 2012):

$$f_{HA} = \frac{1}{\frac{V_W}{m_{DOM} \cdot K_{HA}} + 1} \quad (5)$$

The error in the determination of K_{fw} , K_{HA} and f_{HA} was calculated from the instrumental error in the determination of m_F , m_W , m_{TOT} and m_{DOM} using the error propagation rule (Miller and Miller 2000).

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3 Results and discussion

3.1 ES-HA complex formation

The formation of ES-HA complexes was quantified as a function of pH and HA concentration in order to evaluate the influence of solute-solute interactions on ES retention in the presence of HA. The HA-water partition coefficient K_{HA} for ES was determined using the nd-SPME method described in Section 2.5 and the fraction of ES bound to HA, f_{HA} hence complex formation, was calculated with equation 5. In order to determine K_{HA} , the SPME fibres were calibrated to obtain the fibre-water partition coefficient K_{fw} for ES as a function of pH.

3.1.1. Fibre calibration and determination of fibre partitioning coefficient

SPME has been largely employed as a technique for extracting organic micropollutants from aqueous solutions and values of K_{fw} for α -ES and β -ES are available in the literature (Valor et al. 2001). However, there are no data published on the variation of K_{fw} with pH for ES. Moreover, the free-standing fibre method used in this study differs from the traditionally employed techniques using fibre holders. Fibre calibration was therefore required to establish equilibrium time and determine K_{fw} . PA fibres reached equilibrium after 48 hours and 96 hours were chosen for determination of the partitioning coefficients. No adsorption of ES to the glass was measured in control samples.

PA fibre uptake was constant with pH up to pH 8 and then decreased rapidly (Figure 1). Since ES does not dissociate, this was attributed to the hydrolysis of α -ES and β -ES to ES-diol, which has lower log K_{ow} and therefore less affinity to the fibres (DiFilippo and Eganhouse 2010). However, the decrease at pH 10 and 12 can be considered negligible once the logarithm is calculated, since the difference was less than 0.5 log units, and log K_{fw} for ES can be considered constant with pH

(Figure 1). For the pH range studied the negligible-depletion condition $K_{fw} \cdot \frac{V_F}{V_W} \ll 1$ was fulfilled

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(Vaes et al. 1997). Values of log K_{fw} obtained for ES are in agreement (maximum difference 0.3 log units) with the values obtained in the literature for PA coated fibres at neutral pH (Valor et al. 2001), confirming the validity of the nd-SPME technique employed in this study.

(FIGURE 1)

3.1.2. Determination of HA partition coefficient and percentage of ES bound to HA

The HA partition coefficient for ES, K_{HA} , was estimated as a function of pH and HA concentration. While K_{oc} values for ES have been determined for various soils (Hillenbrand et al. 2006, Ministerio de Agricultura Pesca Y Alimentacion 1999, Organization for Economic Cooperation and Development 1995), there are no published data on partitioning coefficient of ES and aquatic organic matter. Values obtained for soil organic carbon cannot be used for aquatic HA as partition coefficients in water could be 2-3 orders of magnitude greater (Devitt and Wiesner 1998). It is fundamental to quantify the partition coefficients at the same conditions used during the experiments with membranes as environmental conditions have shown to influence considerably the K_{HA} values (DiFilippo and Eganhouse 2010).

As shown in Figure 2, the partitioning coefficient for ES between HA and water and the fraction of ES bound to HA can be considered constant with pH. Albeit HA deprotonates at pH above 4, the complexation of ES and HA did not decrease at high pH as ES is neutral in the whole pH range, in agreement with findings for other organochloride pesticides (Prosen et al. 2002). Log K_{HA} decreased with increasing HA concentration indicating that complexation is limited by the mass of ES available. The percentage of ES bound to HA, calculated with equation 5, increased with HA concentration.

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(FIGURE 2)

3.2 Influence of pH and HA concentration on ES retention

The influence of HA on the removal of ES for different micropollutant MW/membrane MWCO ratio was investigated. Firstly, ES retention was determined with and without HA for TFC-SR2 and TFC-SR3 as a function of pH and secondly, ES retention was determined for the TFC-SR2 and TFC-SR3 as a function of HA concentration. The study of ES retention as a function of pH is important because, while pH was shown not to influence ES-HA complex formation and the percentage of ES bound to HA (Figure 2a), it can influence membrane charge within the pores (Braghetta et al. 1997, Dalwani et al. 2011, 2010). ES retention in the presence of HA was expected to be affected by HA concentration since HA concentration influenced the formation of ES-HA complexes and the percentage of ES bound to HA (Figure 2b).

3.2.1. Influence of pH on ES retention

The permeate flux J_v/J_0 ratio, an indicator of membrane fouling, the ES mass adsorption on the membrane and the ES retention were determined for a pH range between 4 and 12, as shown in Figure 3. The use of new membrane coupons with pure water flux varying $\pm 15\%$, resulted in $\pm 8\%$ variability in retention results and $\pm 0.02 \mu\text{g}/\text{cm}^2$ variability in adsorption results as determined by repeating some experiments in duplicate and triplicate with different membrane coupons. The determined variability was used for all the experiments in this study.

(FIGURE 3)

Figure 3a shows that, for both membranes, J_v/J_0 was constant with pH when ES was filtered alone, showing no effect of pH on the membrane permeate flux. When ES and HA were both filtered, fouling (i.e. J_v/J_0 decline) was not observed for both membranes when compared to J_v/J_0 with ES

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only. For the "tighter" TFC-SR3 (Table 2) the presence of HA did not influence the flux ratio, while for the "looser" TFC-SR2 (Table 2) HA increased the flux ratio at pH 6, 8 and 10 up to 40%. Increased permeate flux in the presence of NOM at pH > 4 has been previously observed for "loose" NF membranes (Braghetta et al. 1997, Schäfer et al. 2010). Since NOM enhances the negative charge of the NF membranes, which increases the electrostatic repulsion within the membrane pores, it was inferred that NOM might increase membrane MWCO (Braghetta et al. 1997, Childress and Elimelech 1996).

(TABLE 2)

ES adsorption onto the TFC-SR3 was low (average over pH: $0.01 \mu\text{g}/\text{cm}^2$) and independent of pH and the presence of HA (Figure 3b). ES adsorption was higher (average over pH: $0.03 \mu\text{g}/\text{cm}^2$) for the more hydrophobic TFC-SR2 (Table 2) compared to the TFC-SR3. At pH > 8, ES adsorption decreased with and without HA for the TFC-SR2. In this pH range ES hydrolyses to ES-diol, which is less hydrophobic than α -ES and β -ES (Table 1) and might adsorb less on the membrane (Banasiak 2009).

For both membranes in the absence of HA ES retention varied with pH (Figure 3c). It is inferred that the variation of membrane surface characteristics with pH (i.e., negative surface charge increase with increase of pH) combined with hydrolyzation of ES isomers to ES-diol, which has a lower molecular weight and lower hydrophobicity, decreased ES retention by the TFC-SR3 membrane with increasing pH. The same occurred for the TFC-SR2 membrane with the exception of pH 12. At this pH it is possible that some of the ES diol is dissociated (pKa value in Table 1) which might have an enhanced retention by the negatively charged membrane.

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For TFC-SR3 (micropollutant MW/membrane MWCO ratio > 1) HA increased ES retention at every pH. This increase in retention is not caused by pore clogging from HA, since J_v/J_o did not decrease when HA was present compared to filtration without HA (Figure 3a). A possible explanation for the increase in ES retention is the formation of ES-HA complexes: as HA is highly retained by the NF membrane, ES molecules that complex with HA will also be retained. The influence of complexation on ES retention will be studied in detail in the next section.

In contrast, ES retention in the presence of HA decreased at pH 6, 8 and 10 and was similar at pH 4 and 12 for the TFC-SR2 (micropollutant MW/membrane MWCO ratio < 1). Decrease in ES retention in the presence of HA was observed for the "loose" membrane, confirming the inferred correlation between micropollutant MW/membrane MWCO ratio and micropollutant removal in the presence of NOM. Decreased ES retention in the presence of HA at pH 6, 8 and 10 for TFC-SR2 corresponded to an increase in flux ratio (Figure 3a), as observed in previous studies (Boussahel et al. 2002, Schäfer et al. 2010), and to an increase in ES adsorption (Figure 3b). At pH 12, the flux was unchanged (Figure 3a) and the ES adsorption on the membrane was lower, translating into an increased retention of ES.

Two mechanisms of ES removal in the presence of HA can be identified so far: (1) for TFC-SR3 the presence of HA increased ES retention, potentially caused by the formation of ES-HA complexes (2) for TFC-SR2 the presence of HA decreased ES retention and increased J_v/J_o for certain pH conditions (pH 6 to 10), indicating a change of membrane performance when HA is present, whilst for others (pH 4 and 12) it increased ES retention, potentially caused by the formation of ES-HA complexes.

3.2.2. Influence of HA concentration on ES retention

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In order to carry out a more in depth investigation of the role of ES-HA complexes on ES removal, retention of ES as a function of HA concentration was studied. For both membranes ES retention as a function of HA concentration was studied at pH 4 because membranes and HA are neutral and charge effects are minimal. ES retention was also investigated at pH 8 for the TFC-SR2, where the presence of HA was found to decrease ES retention (Figure 3c). ES retention as a function of HA concentration at pH 8 was not studied for the TFC-SR3 as ES retention in the presence of HA is independent of pH (Figure 3c).

At pH 4, flux ratio decline occurred for both membranes for HA > 50 mgC/L (Figure 4a). For these experimental conditions the high concentrations of HA caused the membrane to foul by pore blocking (Xu et al. 2005). In this case, ES retention can be affected by pore blocking, competition of adsorption sites between HA deposits and ES (Yoon et al. 2006), and interactions between ES and the fouling layer. The complexity of the mechanisms when the HA fouling layer is present does not allow the study of the impact of ES-HA complexes on ES retention. Therefore, the mechanisms of ES retention in the presence of HA when the HA fouling layer is present will not be discussed in detail further since an investigation of the impact of fouling mechanisms in micropollutant retention is outside the scope of this study. For HA ≤ 50 mgC/L there was no effect on the flux ratio J_v/J_o for both TFC-SR2 and TFC-SR3.

(FIGURE 4)

For the TFC-SR2 at pH 8, the flux ratio increased from 0.97 to 1.21 for HA > 5 mgC/L confirming what was observed previously in Figure 3a. Some studies in the literature have reported an increase in permeate flux after NOM filtration and inferred that it could be linked to increase in MWCO (Braghetta et al. 1997, Childress and Elimelech 1996, Xu et al. 2005, Xu et al. 2006). The influence of HA filtration on MWCO will be studied in detail in the next section.

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ES adsorption was independent of HA concentration for TFC-SR3, while for TFC-SR2 it increased with HA concentration up to HA 50 mgC/L and then decreased for a concentration higher than 50 mgC/L (Figure 4b). The decrease in ES adsorption for HA > 50 mgC/L might be caused either by a higher percentage of ES bound to HA (Figure 2 b) leaving less freely dissolved ES to adsorb on the membrane or due to fouling of the membrane by HA (Figure 4 a) which competes for adsorption sites on the membrane (Yoon et al. 2006). An increase in ES adsorption for HA > 5 mgC/L can be caused by the inferred increase in the MWCO of the membrane due to HA filtration. Micropollutants have been shown to adsorb inside the NF membrane pores (Kimura et al. 2003, Semiao and Schäfer 2012). Hence whilst HA fouling blocks the pores and does not allow for the ES to adsorb inside the TFC-SR2, an increase of MWCO increases the internal area for more ES adsorption to occur.

At pH 4 ES retention increased with HA concentration for the looser TFC-SR2 from 60.0% to 84.4% while it was constant for the tighter TFC-SR3 with a retention of 96.0%. (Figure 4c). For TFC-SR2 at pH 8 ES retention decreased with HA concentration up to HA 50 mgC/L from 55% to 30%, confirming what was observed for HA 12.5 mgC/L at pH 6, 8 and 10 (Figure 3c).

These results confirmed that the presence of HA increased the retention of pesticide ES for TFC-SR3, whose MWCO is smaller than ES MW, and decreased ES retention for TFC-SR2 at pH 8, whose MWCO is bigger than ES MW. However, ES retention by TFC-SR2 was found to increase at pH 4 with increase of HA concentration. HA concentration and pH played a role in the different ES retention in the presence of HA. HA concentration influenced ES-HA interactions and pH affected HA-membrane interactions.

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ES adsorption on the membranes (ES-membrane interactions) was not believed to influence ES retention in the presence of HA. ES adsorption values on TFC-SR2 were similar at pH 4 and at pH 8 (Figure 4b) for HA concentrations <12.5 mgC/L while ES retention in the presence of HA increased at pH 4 and decreased at pH 8 (Figure 4c). To elucidate the mechanisms responsible for increase/decrease of ES retention in the presence of HA, the contributions of solute-solute interactions (ES-HA complexes) and solute-membrane (HA-membrane) interactions on ES removal have been investigated and described in Section 3.3.

3.3 Mechanisms of ES retention in presence of HA

In order to quantify the contribution of ES-HA interactions on ES removal, ES retention in the presence of HA was estimated from the calculated partition coefficient, K_{HA} , and the fraction of ES bound to HA, f_{HA} . The approach developed by Neale and Schäfer (2012) for UF was modified for NF. Neale and Schäfer (2012) determined hormone retention in the presence of HA as proportional to the retention of HA and to the fraction of micropollutant bound to HA only, due to the low retention of hormones by UF membranes. In the case of NF, micropollutant retention cannot be ignored and the method was modified and improved by carrying out a mass balance in order to take this term into account.

Some assumptions were made to determine the fraction of ES bound to HA and therefore estimate retention due to complex formation:

- (1) The total mass of ES in solution (m_{ES}) is either freely dissolved (m_{ES}) or complexed to HA (m_{ES-HA}) after the membrane saturation has been reached:

$$m_{ES} = m_{ES-HA} + m_{ES} \quad (6)$$

- (2) ES complexed with HA is retained together with the HA to which it is partitioned
- (3) ES freely dissolved in HA solution has the same retention as ES during experiments without HA carried out at the same conditions of pH, pressure and background electrolyte.

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While the first two assumptions can be considered generally valid, the last assumption will not be true if the presence of HA influences the retention of freely dissolved ES. HA-membrane interactions can influence the retention of freely dissolved ES in the HA solution and result in different overall ES retention than the estimated retention. HA can adsorb to the membrane surface resulting in pore blocking (Xu et al. 2005) and increasing membrane charge (Hong and Elimelech 1997, Xu et al. 2005), membrane MWCO (Xu et al. 2006) and membrane hydrophilicity (Hong and Elimelech 1997, Schäfer et al. 2010).

The total ES retention due to the retention of ES complexed with HA and freely dissolved ES has been estimated by mass balance from the total mass of ES in the feed (m_{ESfeed}) and in the permeate (m_{ESperm}):

$$m_{ESfeed} = m_{ES-HAfeed} + m_{IESfeed} = f_{HA} \cdot m_{ESfeed} + (1 - f_{HA}) \cdot m_{ESfeed} \quad (7)$$

$$m_{ESperm} = m_{ES-HAperm} + m_{IESperm} = (1 - R_{HA}) \cdot m_{ES-HAfeed} + (1 - R_{ES}) \cdot m_{IESfeed} \quad (8)$$

where R_{HA} is the retention of HA and R_{ES} is the retention of ES during experiments without HA.

For TFC-SR3, R_{HA} was 99% and could be considered constant with pH and HA concentration ($\pm 2\%$ variability); for TFC-SR2, the average HA retention over the pH was 88%, increasing from 75.8% at pH 4 to 98.5% at pH 12 and from 71.5% for HA concentration 5 mgC/L to 99.1% for HA 250 mgC/L.

The retention estimated with this methodology is indicated with a dotted line in Figure 3c and Figure 4c, and was compared with the retention obtained during ES-HA experiments. Similar experimental and estimated retention would indicate that solute-membrane interactions are negligible (i.e. the third hypothesis is verified) and solute-solute interactions are dominant. When

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solute-membrane interactions are important the retention predicted from K_{HA} is expected to be different from the retention obtained experimentally. This methodology depends on the fraction of micropollutant bound to NOM, on micropollutant retention and on NOM retention and it can be applied to any micropollutant that forms complexes with NOM to estimate the contribution of micropollutant-NOM interactions on micropollutant retention by NF, irrespective of the type of interactions and the compound properties.

As shown in Figure 3c, ES retention in the presence of HA estimated with K_{HA} was similar (maximum 10% difference) to the experimental retention for the TFC-SR3, showing that for this membrane solute-solute interactions (i.e. the formation of ES-HA complexes) are the dominant mechanism affecting ES retention. For TFC-SR2 the estimated retention was higher than the experimental retention for all the pH range studied, with the exception of pH 4 and 12, indicating that solute-membrane interactions (i.e. HA-membrane interactions) played a role. For both membranes at pH 4 the estimated ES retention was similar to the experimental retention (Figure 4c), indicating that at this pH solute-solute interactions are the dominant mechanism.

For TFC-SR2 at pH 8 ES retention obtained experimentally was lower than the estimated ES retention for any HA concentration (Figure 4c). At this pH the role of solute-membrane interactions on ES removal was more predominant than the formation of ES-HA complexes. The U-shape of the retention curve indicated that solute-membrane interactions were dominant for lower HA concentrations while at high HA concentrations both ES-HA interactions and pore blocking by HA fouling (evidenced from a decrease in permeate flux in Figure 4a) became more important. However, even at high HA concentrations ES retention was lower than the estimated retention (dotted line) since solute-membrane interactions could not be considered negligible.

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In order to establish how solute-membrane interactions affected ES retention in the presence of HA, the characteristics of both membranes were evaluated for membranes pre-filtered with 900 mL of ultra-pure water and background electrolyte and membranes pre-filtered with 900 mL of solution containing 12.5 mgC/L of HA and background electrolyte at pH 8. Membrane MWCO and contact angle were determined in order to evaluate change in membrane pore size and hydrophilicity caused by the presence of HA (Table 3).

(TABLE 3)

HA deposited preferentially on the TFC-SR3, forming a visible yellowish layer on the membrane, while visible HA deposits were not observed on the TFC-SR2. This different behaviour does not seem to be linked with the different roughness of the two membranes (Table 2), as the membrane with the highest roughness had no visible deposits on its surface. MWCO increased in the presence of HA for both membranes, confirming what was inferred in previous studies (Xu et al. 2005, Xu et al. 2006). The increase in MWCO for TFC-SR3 did not influence ES retention as the higher MWCO (179 g/mol) was still lower than ES MW (407 g/mol). In the case of TFC-SR2, for which micropollutant MW/membrane MWCO ratio < 1 and ES is partially retained, the increase in MWCO from 460 to 496 g/mol decreased the ratio further, in turn decreasing ES retention.

After HA were filtered the observed contact angle decreased for TFC-SR2 and increased for TFC-SR3 (Table 3). For membranes fouled by NOM, contact angle measurements have been shown to be representative of the fouling layer: in the case of fouling by HA, contact angles indicated the adhesion of a layer of intermediate hydrophobicity (Jucker and Clark 1994, Lee et al. 2004, Palacio et al. 1999, Xu et al. 2006). For TFC-SR3 the contact angle is thought to be determined by the HA layer visibly deposited on the membrane after filtration; the roughness of the HA deposits were also likely to increase the observed contact angle (de Gennes 1985). For TFC-SR2, for which HA

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deposits were not visible after filtration, the contact angle is thought to reflect membrane hydrophilization due to filtration of charged HA (Hong and Elimelech 1997). Increase in hydrophilization can also explain the observed increase in permeate flux (Figure 4a).

A schematic of the proposed mechanisms is presented in Figure 5. At pH 4, when membranes and HA are neutrally charged, size exclusion and solute-solute interactions (i.e. ES-HA interactions) dominated ES retention. At neutral pH, both HA and the membranes are negatively charged and solute-membrane interactions (i.e. HA-membrane interactions) influence membrane MWCO and hydrophilicity. The filtration of HA increased the MWCO for both membranes (Table 3), but different trends were obtained. For TFC-SR3, whose micropollutant MW/membrane MWCO ratio > 1, the small increase in MWCO from 165 to 179 g/mol was not sufficient to allow for increase in ES passage. This low HA impact in MWCO increase was further evidenced by a lack of increase in permeate flux (Figure 3 a and Figure 4 a). For TFC-SR3, the formation of ES-HA complexes was the dominant mechanism responsible for the increase of ES retention and it overcame the increase in MWCO (Figure 3 c). For TFC-SR2, interactions between charged HA and the membrane also resulted in an increase of the MWCO (Table 3), which is further evidenced from an increase in permeate flux (Figure 3 a and Figure 4 a). As TFC-SR2 has a micropollutant MW/membrane MWCO < 1, a further increase in the MWCO had a high impact in ES retention by decreasing it considerably. For TFC-SR2, HA-membrane interaction was the dominant mechanism responsible for the decrease of ES retention when HA are present since the formation of HA-ES complexes did not overcome the increase of membrane MWCO.

(FIGURE 5)

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4 Conclusions

The mechanisms involved in the removal of micropollutants by NF membranes in the presence of NOM were identified and evaluated in this study. For the first time, the contribution of both solute-solute interactions and solute-membrane interactions were evaluated to explain micropollutant retention mechanisms.

Results showed that in the absence of HA-membrane interactions, ES-HA complexation was the governing mechanism in ES removal, enhancing ES removal. ES-membrane interactions did not contribute to the variation of ES retention in the presence of HA. In contrast, HA-membrane interactions affected membrane performance by increasing the MWCO and decreasing ES retention.

This work improves the understanding of the fundamentals involved in the removal mechanisms by NF and demonstrates that the evaluation of the contributions of both solute-solute interactions and solute-membrane interactions is fundamental for understanding micropollutant removal mechanisms by NF

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List of Figures

Figure 1 Mass of ES in the nd-SPME fibre for different ES concentrations and Log K_{fw} values for ES as function of pH. ES 10, 25, 50, 100 $\mu\text{g/L}$, background electrolyte 1 mM NaHCO_3 and 20 mM NaCl .

Figure 2 HA-water partition coefficient and fraction of ES bound to HA (a) as a function of pH, HA 12.5 mgC/L and (b) as a function of HA concentration. ES 10, 25, 50, 100 $\mu\text{g/L}$, background electrolyte 1 mM NaHCO_3 and 20 mM NaCl .

Figure 3 (a) Ratio of permeate flux J_v and initial pure water flux J_0 (b) ES adsorption (c) and ES retention as a function of pH for TFC-SR2 and TFC-SR3. Dotted lines indicate ES retention in presence of HA estimated using the calculated partition coefficient K_{HA} . ES 10 $\mu\text{g/L}$, HA 12.5 mgC/L, pressure 5 bar, background electrolyte 1 mM NaHCO_3 and 20 mM NaCl .

Figure 4 (a) Ratio of permeate flux J_v and initial pure water flux J_0 (b) ES adsorption and (c) ES retention as a function of HA concentration for TFC-SR2 and TFC-SR3. Dotted lines indicate ES retention in presence of HA estimated using the calculated partition coefficient K_{HA} . ES 10 $\mu\text{g/L}$, pressure 5 bar, HA 5, 7.5, 12.5, 25 50, 125 250 mgC/L, background electrolyte 1 mM NaHCO_3 and 20 mM NaCl .

Figure 5 Conceptual sketch (to scale) of main retention mechanisms for freely dissolved ES (MW 407 g/mol) and ES-HA complexes by TFC-SR2 and TFC-SR3. The presence of HA increases the MWCO for both membranes at pH 8 (changes indicated by the lighter area on the membranes). For TFC-SR3, MWCO increases from 165 to 179 g/mol but the passage of ES decreases due to the formation of ES-HA complexes: solute-solute interactions are the main mechanism of ES retention

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in the presence of HA. For TFC-SR2, MWCO increases from 460 to 496 g/mol causing an increase

in the passage of ES despite the formation of ES-HA complexes: solute-membrane interactions are the dominant mechanism.

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List of Tables

Table 1 – Characteristics of pesticide Endosulfan

Table 2 – Characteristics of TFC-SR2 and TFC-SR3

Table 3 – Membrane characteristics for a membrane pre-filtered with 900 mL of ultra-pure water and background electrolyte and a membrane through which 12.5 mgC/L of HA and background electrolyte have been filtered at pH 8

Table 1

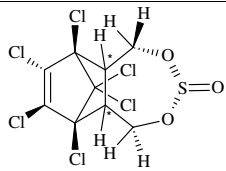
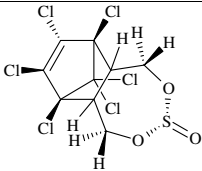
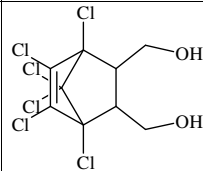
	α-ES	β-ES	Endosulfan diol
			
Formula	C ₉ H ₆ Cl ₆ O ₃ S	C ₉ H ₆ Cl ₆ O ₃ S	C ₉ H ₈ Cl ₆ O ₂
Molecular Weight (g/mol)	406.93	406.93	360.88
Log K _{ow}	3.83 (Hansch et al. 1995)	3.83 (Hansch et al. 1995)	3.68 (Banasiak 2009)
pK _a	-	-	14.62–15.22 (Banasiak 2009)
Dipole Moment	1.02 (Forman et al. 1965)	3.18 (Forman et al. 1965)	Not available

Table 2

	Material	MWCO ¹ (g/mol)	Estimated pore radius (nm)	Point of zero charge ² (pH)	Contact Angle (°)	Roughness ³ (nm)
TFC-SR2	Polyamide on	460	0.52	4.25	57	17.9
TFC-SR3	polysulfone	165	0.38	3.84	44	5.2

¹pressure 5 bar, neutral pH

²Electrolyte solution 1 mM NaHCO₃ and 20 mM NaCl

³ Average roughness, R_a

Table 3

	TFC-SR2		TFC-SR3	
Pre-filtration Method	Ultra-pure water and electrolyte ¹	HA and electrolyte ¹	Ultra-pure water and electrolyte ¹	HA and electrolyte ¹
MWCO (g/mol)	460	496	165	179
Contact angle	57	49	44	59

¹Electrolyte solution 1 mM NaHCO₃ and 20 mM NaCl

Figure 1

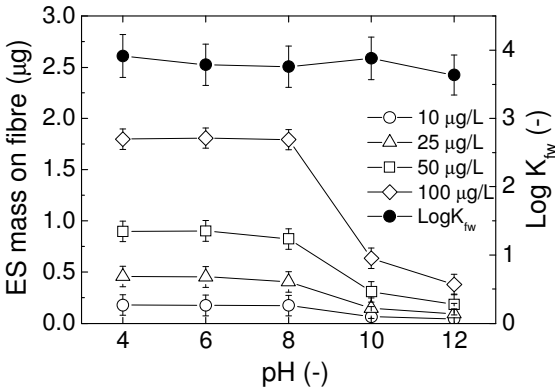


Figure 2

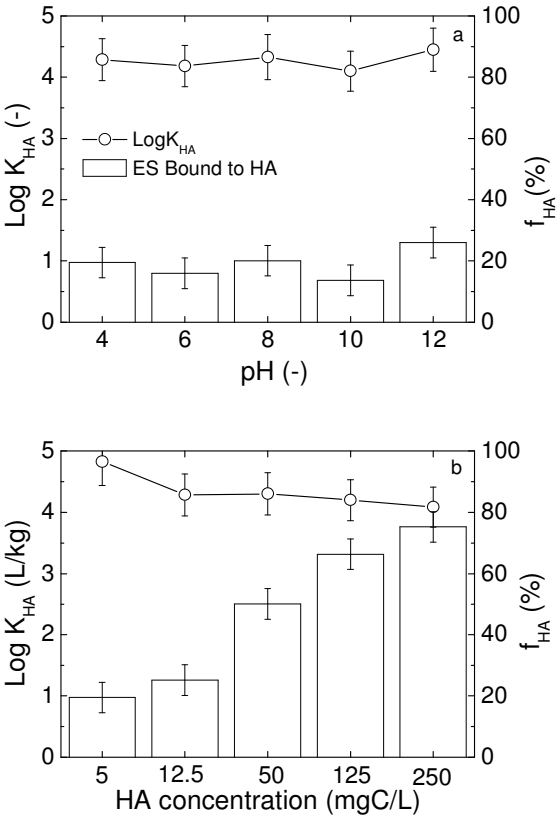


Figure 3

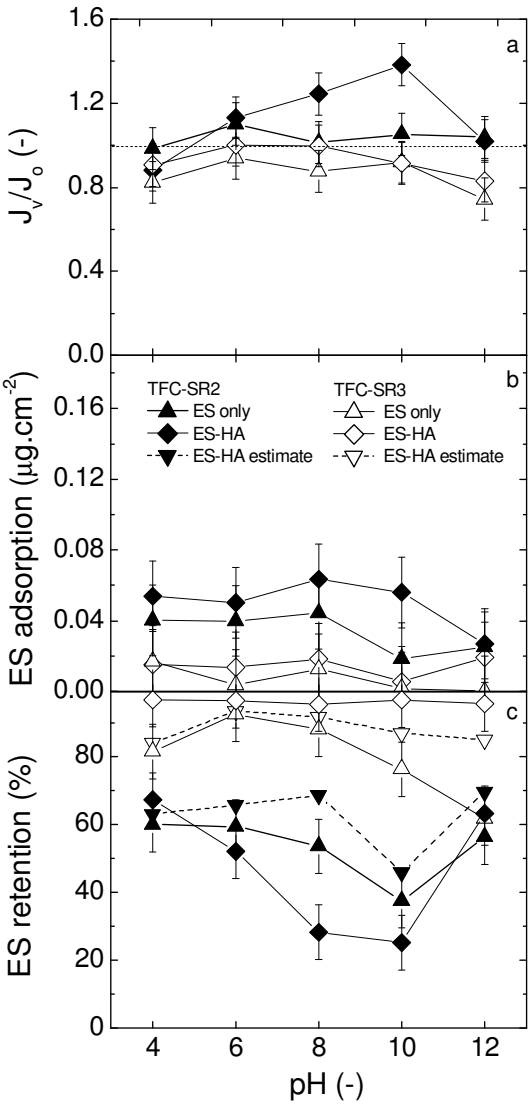


Figure 4

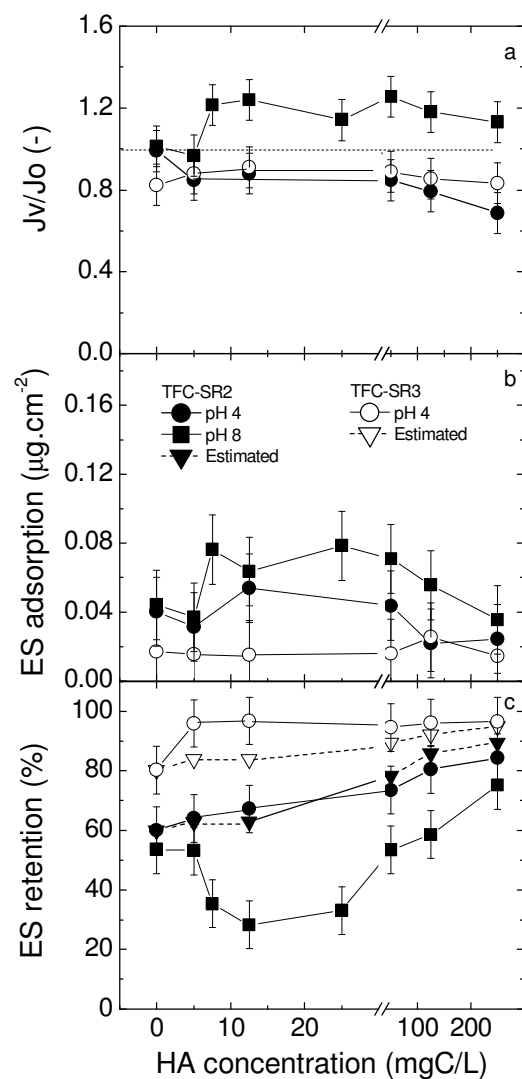


Figure 5

